

09/147914

Practitioner's Docket No. U 012130-1

CHAPTER II

TRANSMITTAL LETTER
TO THE UNITED STATES ELECTED OFFICE (EO/US)
(ENTRY INTO U.S. NATIONAL PHASE UNDER CHAPTER II)

| INTERNATIONAL APPLICATION NO. CLAIMED | INTERNATIONAL FILING DATE | PRIORITY | DATE |
|---|---------------------------|----------|----------------|
| PCT/US97/17774 | 2 OCTOBER 1997 | | 9 OCTOBER 1996 |
| TITLE OF INVENTION A PROCESS FOR THE RECOVERY OF LACTIC ACID FROM AQUEOUS LACTATE SALT SOLUTIONS, INVOLVING THE USE OF ION EXCHANGERS | | | |
| APPLICANT(S) | | | |
| 1. AHARON MEIR EYAL | | | |
| 2. PONNAMPALAM ELANKOVN | | | |

Box PCT
Assistant Commissioner for Patents
Washington D.C. 20231
ATTENTION: EO/US

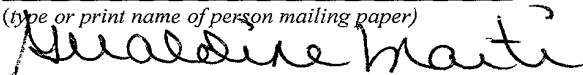
NOTE: *The completion of those filing requirements that can be made at a time later than 30 months from the priority date results from the Commissioner exercising his judgment under the authority granted under 35 USC 371(d). The filing receipt will show the actual date of receipt of the last item completing the entry into the national phase. See 37 C.F.R. §1.491 which states: "An international application enters the national state when the applicant has filed the documents and fees required by 35 USC 371(c) within the periods set forth in § 1.494 and § 1.495."*

WARNING: *Where the items are those which can be submitted to complete the entry of the international application into the national phase are subsequent to 30 months from the priority date the application is still considered to be in the international state and if mailing procedures are utilized to obtain a date the express mail*

CERTIFICATION UNDER 37 C.F.R. 1.10*
(Express Mail label number is mandatory.)
(Express Mail certification is optional.)

I hereby certify that this correspondence and the documents referred to as attached therein are being deposited with the United States Postal Service on this date MARCH 23, 1999, in an envelope as "Express Mail Post Office to Addressee," Mailing Label Number EE784103425US, addressed to the: Assistant Commissioner for Patents, Washington, D.C. 20231.

GERALDINE MARTI
(type or print name of person mailing paper)


Signature of person mailing paper

WARNING: *Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.*

***WARNING:** *Each paper or fee filed by "Express Mail" must have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. 1.10(b)*
"Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will not be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442.

(Transmittal Letter to the United States Elected Office (EO/US)—page 1 of 8)

EE 78 41 034 25 US

procedure of 37 C.F.R. §1.10 must be used (since international application papers are not covered by an ordinary certificate of mailing - See 37 C.F.R. §1.8.

NOTE: Documents and fees must be clearly identified as a submission to enter the national state under 35 USC 371 otherwise the submission will be considered as being made under 35 USC 111. 37 C.F.R. § 1.494(f).

1. Applicant herewith submits to the United States Elected Office (EO/US) the following items under 35 U.S.C. 371:

- a. ☒ This express request to immediately begin national examination procedures (35 U.S.C. 371(f)).
- b. ☒ The U.S. National Fee (35 U.S.C. 371(c)(1)) and other fees (37 C.F.R. § 1.492) as indicated below:

2.Fees

| CLAIMS FEE | (1) FOR | (2) NUMBER FILED | (3) NUMBER EXTRA | (4) RATE | (5) CALCULATIONS |
|--------------|---|------------------|------------------|--------------|------------------|
| []* | TOTAL CLAIMS | 34 - 20 = | 14 | x \$ 18.00 = | \$ 252.00 |
| | INDEPENDENT CLAIMS | 2 - 3 = | 0 | x \$ 78.00 = | 0.00 |
| | MULTIPLE DEPENDENT CLAIM(S) (if applicable) + \$260.00 | | | | |
| BASIC FEE** | <input type="checkbox"/> U.S. PTO WAS INTERNATIONAL PRELIMINARY EXAMINATION AUTHORITY Where an International preliminary examination fee as set forth in § 1.482 has been paid on the international application to the U.S. PTO: <input type="checkbox"/> and the international preliminary examination report states that the criteria of novelty, inventive step (non-obviousness) and industrial activity, as defined in PCT Article 33(2) to (4) have been satisfied for all the claims presented in the application entering the national stage (37 CFR 1.492(a)(4)) \$96.00 <input type="checkbox"/> and the above requirements are not met (37 CFR 1.492(a)(1)) \$670.00 <input checked="" type="checkbox"/> U.S. PTO WAS NOT INTERNATIONAL PRELIMINARY EXAMINATION AUTHORITY Where no international preliminary examination fee as set forth in § 1.482 has been paid to the U.S. PTO, and payment of an international search fee as set forth in § 1.445(a)(2) to the U.S. PTO: <input type="checkbox"/> has been paid (37 CFR 1.492(a)(2)) \$760.00 <input type="checkbox"/> has not been paid (37 CFR 1.492(a)(3)) \$970.00 <input checked="" type="checkbox"/> where a search report on the international application has been prepared by the European Patent Office or the Japanese Patent Office (37 CFR 1.492(a)(5)) \$840.00 | | | | |
| | Total of above Calculations | | | | = 1,092.00 |
| SMALL ENTITY | Reduction by ½ for filing by small entity, if applicable. Affidavit must be filed. (note 37 CFR 1.9, 1.27, 1.28) | | | | - |
| | Subtotal | | | | 1,092.00 |
| | Total National Fee | | | | \$ 1,092.00 |
| | Fee for recording the enclosed assignment document \$40.00 (37 CFR 1.21(h)). (See Item 13 below). See attached "ASSIGNMENT COVER SHEET". | | | | |
| TOTAL | Total Fees enclosed | | | | \$ 1,092.00 |

*See attached Preliminary Amendment Reducing the Number of Claims.

- i. ☒ A check in the amount of \$1,092.00 to cover the above fees is enclosed.
- ii. ☐ Please charge Account No. _____ in the amount of \$ _____.
A duplicate copy of this sheet is enclosed.

****WARNING:** "To avoid abandonment of the application the applicant shall furnish to the United States Patent and Trademark Office not later than the expiration of 30 months from the priority date: * * * (2) the basic national fee (see § 1.492(a)). The 30-month time limit may not be extended." 37 C.F.R. § 1.495(b).

WARNING: If the translation of the international application and/or the oath or declaration have not been submitted by the applicant within thirty (30) months from the priority date, such requirements may be met within a time period set by the Office. 37 C.F.R. § 1.495(b)(2). The payment of the surcharge set forth in § 1.492(e) is required as a condition for accepting the oath or declaration later than thirty (30) months after the priority date. The payment of the processing fee set forth in § 1.492(f) is required for acceptance of an English translation later than thirty (30) months after the priority date. Failure to comply with these requirements will result in abandonment of the application. The provisions of § 1.136 apply to the period which is set. Notice of Jan. 3, 1993, 1147 O.G. 29 to 40.

3. ☒ A copy of the International application as filed (35 U.S.C. 371(c)(2)):

NOTE: Section 1.495 (b) was amended to require that the basic national fee and a copy of the international application must be filed with the Office by 30 months from the priority date to avoid abandonment "The International Bureau normally provides the copy of the international application to the Office in accordance with PCT Article 20. At the same time, the International Bureau notifies applicant of the communication to the Office. In accordance with PCT Rule 47.1, that notice shall be accepted by all designated offices as conclusive evidence that the communication has duly taken place. Thus, if the applicant desires to enter the national stage, the applicant normally need only check to be sure the notice from the International Bureau has been received and then pay the basic national fee by 30 months from the priority date." Notice of Jan. 7, 1993, 1147 O.G. 29 to 40, at 35-36. See item 14c below.

- a. ☒ is transmitted herewith.
- b. ☒ is not required, as the application was filed with the United States Receiving Office.
- c. ☐ has been transmitted
 - i. ☐ by the International Bureau.
Date of mailing of the application (from form PCT/IB/308): _____.
 - ii. ☐ by applicant on _____.
Date

4. ☒ A translation of the International application into the English language (35 U.S.C. 371(c)(2)):

- a. ☐ is transmitted herewith.
- b. ☒ is not required as the application was filed in English.
- c. ☐ was previously transmitted by applicant on _____.
Date
- d. ☐ will follow.

5. ☒ Amendments to the claims of the International application under PCT Article 19 (35 U.S.C. 371(c)(3)):

NOTE: The Notice of January 7, 1993 points out that 37 C.F.R. § 1.495(a) was amended to clarify the existing and continuing practice that PCT Article 19 amendments must be submitted by 30 months from the priority date and this deadline may not be extended. The Notice further advises that: "The failure to do so will not result in loss of the subject matter of the PCT Article 19 amendments. Applicant may submit that subject matter in a preliminary amendment filed under section 1.121. In many cases, filing an amendment under section 1.121 is preferable since grammatical or idiomatic errors may be corrected." 1147 O.G. 29-40, at 36.

- a. ☐ are transmitted herewith.
- b. ☐ have been transmitted
- i. ☐ by the International Bureau.
Date of mailing of the amendment (from form PCT/IB/308): _____.
- ii. ☐ by applicant on _____.
Date
- c. ☒ have not been transmitted as
- i. ☒ applicant chose not to make amendments under PCT Article 19.
Date of mailing of Search Report (from form PCT/ISA/210): _____.
- ii. ☐ the time limit for the submission of amendments has not yet expired.
The amendments or a statement that amendments have not been made will be transmitted before the expiration of the time limit under PCT Rule 46.1.
6. ☒ A translation of the amendments to the claims under PCT Article 19 (38 U.S.C. 371(c)(3)):
- a. ☐ is transmitted herewith.
- b. ☐ is not required as the amendments were made in the English language.
- c. ☒ has not been transmitted for reasons indicated at point 5(c) above.
7. ☒ A copy of the international examination report (PCT/IPEA/409)
- ☒ is transmitted herewith.
- ☐ is not required as the application was filed with the United States Receiving Office.
8. ☒ Annex(es) to the international preliminary examination report
- a. ☐ is/are transmitted herewith.
- b. ☒ is/are not required as the application was filed with the United States Receiving Office.
9. ☒ A translation of the annexes to the international preliminary examination report
- a. ☐ is transmitted herewith.
- b. ☒ is not required as the annexes are in the English language.

10. ☒ An oath or declaration of the inventor (35 U.S.C. 371(c)(4)) complying with 35 U.S.C. 115
- a. ☐ was previously submitted by applicant on _____.
Date
- b. ☐ is submitted herewith, and such oath or declaration
- i. ☐ is attached to the application.
- ii. ☐ identifies the application and any amendments under PCT Article 19 that were transmitted as stated in points 3(b) or 3(c) and 5(b); and states that they were reviewed by the inventor as required by 37 C.F.R. 1.70.
- iii. ☒ will follow.

Other document(s) or information included:

11. ☒ An International Search Report (PCT/ISA/210) or Declaration under PCT Article 17(2)(a):
- a. ☒ is transmitted herewith.
- b. ☐ has been transmitted by the International Bureau.
Date of mailing (from form PCT/IB/308): _____.
- c. ☐ is not required, as the application was searched by the United States International Searching Authority.
- d. ☐ will be transmitted promptly upon request.
- e. ☐ has been submitted by applicant on _____.
Date
12. ☒ An Information Disclosure Statement under 37 C.F.R. 1.97 and 1.98:
- a. ☒ is transmitted herewith.
Also transmitted herewith is/are:
☒ Form PTO-1449 (PTO/SB/08A and 08B).
☒ Copies of citations listed.
- b. ☐ will be transmitted within THREE MONTHS of the date of submission of requirements under 35 U.S.C. 371(c).
- c. ☐ was previously submitted by applicant on _____.
Date
13. ☐ An assignment document is transmitted herewith for recording.

A separate ☐ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.

14. ☒ Additional documents:
- a. ☒ Copy of request (PCT/RO/101)
 - b. ☒ International Publication No. WO 98/15518
 - i. ☒ Specification, claims and drawing
 - ii. ☐ Front page only
 - c. ☐ Preliminary amendment (37 C.F.R. § 1.121)
 - d. ☒ Other
- COPY OF FORM PCT/IB/308: COPY OF FORM PCT/IPEA/401 (DEMAND)
COPY OF FORM PCT/IPEA/408 (WRITTEN OPINION: COPY OF RESPONSE
TO WRITTEN OPINION.
15. ☒ The above checked items are being transmitted
- a. ☒ before 30 months from any claimed priority date.
 - b. ☐ after 30 months.
16. ☐ Certain requirements under 35 U.S.C. 371 were previously submitted by the applicant on _____, namely:
- _____
- _____
- _____

AUTHORIZATION TO CHARGE ADDITIONAL FEES

WARNING: *Accurately count claims, especially multiple dependent claims, to avoid unexpected high charges if extra claims are authorized.*

NOTE: *"A written request may be submitted in an application that is an authorization to treat any concurrent or future reply, requiring a petition for an extension of time under this paragraph for its timely submission, as incorporating a petition for extension of time for the appropriate length of time. An authorization to charge all required fees, fees under § 1.17, or all required extension of time fees will be treated as a constructive petition for an extension of time in any concurrent or future reply requiring a petition for an extension of time under this paragraph for its timely submission. Submission of the fee set forth in § 1.17(a) will also be treated as a constructive petition for an extension of time in any concurrent reply requiring a petition for an extension of time under this paragraph for its timely submission." 37 C.F.R. § 1.136(a)(3).*

NOTE: *"Amounts of twenty-five dollars or less will not be returned unless specifically requested within a reasonable time, nor will the payer be notified of such amounts; amounts over twenty-five dollars may be returned by check or, if requested, by credit to a deposit account." 37 C.F.R. § 1.26(a).*

☒ The Commissioner is hereby authorized to charge the following additional fees that may be required by this paper and during the entire pendency of this application to Account No. 12-0425.

☒ 37 C.F.R. 1.492(a)(1), (2), (3), and (4) (filing fees)

WARNING: *Because failure to pay the national fee within 30 months without extension (37 C.F.R. § 1.495(b)(2)) results in abandonment of the application, it would be best to always check the above box.*

☐ 37 C.F.R. 1.492(b), (c) and (d) (presentation of extra claims)

NOTE: *Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by*

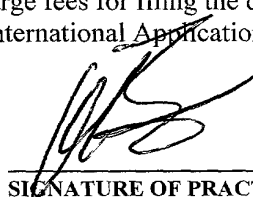
the PTO in any notice of fee deficiency (37 C.F.R. § 1.492(d)), it might be best not to authorize the PTO to charge additional claim fees, except possible when dealing with amendments after final action.

- ☒ 37 C.F.R. 1.17 (application processing fees)
- ☐ 37 C.F.R. 1.17(a)(1)-(5)(extension fees pursuant to § 1.136(a).
- ☐ 37 C.F.R. 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 C.F.R. 1.311(b))

NOTE: Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 C.F.R. § 1.311(b).

NOTE: 37 C.F.R. 1.28(b) requires "Notification of any change in loss of entitlement to small entity status must be filed in the application . . . prior to paying, or at the time of paying . . . issue fee." From the wording of 37 C.F.R. § 1.28(b): (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity.

- ☒ 37 C.F.R. § 1.492(e) and (f) (surcharge fees for filing the declaration and/or filing an English translation of an International Application later than 30 months after the priority date).



SIGNATURE OF PRACTITIONER

Reg. No.: 25,858

WILLIAM R. EVANS

(type or print name of practitioner)

Tel. No.: (212)708-1930

LADAS & PARRY

P.O. Address

26 WEST 61ST STREET

NEW YORK, NEW YORK 10023

Customer No.:

510 Rec'd PCT/PTO 23 MAR 1999

A PROCESS FOR THE RECOVERY OF LACTIC ACID

The present invention relates to a process for the recovery of lactic acid.

More particularly, the present invention relates to a process for the recovery of lactic acid from aqueous solutions containing at least one water-soluble lactate salt and having a pH of about between 4 and 14.

Lactic acid has long been used as a food additive and in various chemical and pharmaceutical applications. More recently, lactic acid has been used in the making of biodegradable polylactic acid polymers as a replacement for present plastic materials, as well as for various new uses where biodegradability is need or desired. Accordingly, there is an ever-increasing demand for lactic acid. The present invention aims at meeting this demand by providing an efficient and environmentally friendly process for producing lactic acid which avoids the consumption of bases and acids and substantially reduces, if not eliminates, the formation of waste or byproduct salts.

The production of lactic acid is commonly carried out by fermentation of a strain of the bacterial genus *lactobacillus delbrueckii* or *Lactobacillus acidophilus*. In general, the production of lactic acid by fermentation in a fermentation broth is well known in the art. The fermentation substrate consists of carbohydrates together with suitable mineral and proteinaceous nutrients. Because the lactic acid-producing microorganisms are inhibited in a

strongly acidic environment, lactic acid fermentation is conducted at about neutral pH and a neutralizing agent is added for pH adjustment. As the pK_a of lactic acid is 3.86, at the pH of fermentation, practically only lactate salts exist. Thus, recovery of lactic acid (in an acid form) from the fermentation liquor requires chemical conversion. Several processes were developed for such conversion.

In some of the processes the conversion liberates lactic acid in solution, e.g. by displacement with a strong acid. Thus, when calcium bases are used as the neutralizing agents in the fermentation, calcium lactate is formed. Reacting the calcium lactate-containing fermentation liquor with sulfuric acid results in precipitation of gypsum and liberation of lactic acid in the solution.

Nakanishi and Tsuda (JP 46/30176) consider production of 1-butyl lactate by extraction of an acidified crude fermentation broth with 1-butanol, followed by esterification of the extract phase. BASF (EP-0159 585) considers a similar process with isobutanol to form isobutyl lactate. The process of WO 93/00440, assigned to DU PONT, comprises the steps of: (1) simultaneously mixing a strong acid, an alcohol, and a concentrated fermentation broth which contains mainly basic salts of lactic acid, which react to form a crystal precipitate comprising basic salts of the strong acid and an impure lactate ester of the alcohol; (2) removing water from the mixture as a water/alcohol azeotrop which can be accomplished either sequentially or substantially simultaneously with step (1); removing the crystal precipitate from the mixture; and (4) distilling the impure lactate ester to remove impurities, and recovering the high purity ester.

Alternatively to purifying the lactic acid, which is liberated by displacement with a strong acid, through esterification and distillation of the ester, one could purify it by extraction. The extractant could be a relatively weak one and would allow the recovery of the extracted HLa at high concentration by back-extraction. The known (and food approved) weak extractants to be considered are amine-based ones or solvating extractants (one may consider esters, ethers, ketones, aldehydes, etc., but alkanols seem preferable).

Out of these two groups, the amine-based ones are more attractive for several reasons: (i) they are more selective and would therefore provide for higher product purity, (ii) their extraction capacity is higher and therefore the extractant flow will be lower, and (iii) the amine-based extractants show the temperature sensitivity of the extraction and therefore provide for the “uphill pumping” through back-extraction, at a temperature which is higher than that of the extraction.

These preferred amine-based extractants would not work in a simple process, where the (stronger than lactic) displacing acid is added to the lactate salt-containing solution and the liberated HLa is directly extracted by contact with the extractant. The amine-based extractant prefers the stronger acid in a mixture and would therefore reverse the reaction (remove the added acid).

Acidulating neutral fermentation liquors by the addition of acids usually results in the formation of by-product salts such as the gypsum ammonium and sodium sulfate. Reagents are consumed and disposal of undesired by-products is required.

Efforts have recently been made to recover lactic acid from fermentation liquors without the formation of such by-products. (Such processes will be referred to in the following as salt splitting processes.) In some recently published patents, liquid liquid extraction (LLE) is applied for salt splitting. Thus, in King's US 5,132,456, a strongly basic extractant extracts part of the lactic acid from the neutral solution, which results in a lactic acid loaded extractant and a basic solution. This basic solution, which still contains most of the lactic acid values, could be recycled as a neutralizing medium to the fermentation. In Baniel's US 5,510,526, the extraction of the acid is conducted under CO₂ pressure so that a bicarbonate is formed. The latter can be used as a neutralizing agent in the fermentation. In order to limit the CO₂ pressure to an economic one and still achieve high yields, the extractant used should be quite strong. Recovery of the extracted lactic acid from such strong extractants is difficult, as they hold strongly to it. Recovery of the extracted acid by washing with an aqueous solution of a base is feasible, but forms the lactate salt of the base. It is therefore not practical in those cases where lactic acid is the desired product. Back-extraction with water forms an overly diluted product.

US 5,132,456 suggests a way for recovering extracted carboxylic acid from a strong extractant. It comprises leaching or back-extraction with an aqueous solution of ammonia or low molecular weight alkyl amine, especially trimethyl amine (TMA). The resultant aqueous ammonium or alkylammonium carboxylate solution can be concentrated, if necessary, and the carboxylate can be decomposed thermally to yield the product carboxylic acid and ammonia or amine which can be condensed and recycled. This process is costly and complex. According to the invention, it is particularly problematic

for recovery of extracted lactic acid: "For lactic acid the decomposition is incomplete, being stopped by the formation of a viscous, almost glassy mass containing polymerized lactic acid along with substantial TMA and water. There are, however, effective ways of driving the decomposition to completion for lactic acid, such as diluting the viscous mass with an appropriate solvent (e.g. methyl isobutyl ketone) and continuing the heating and decomposition process."

With these state of the art in mind there is now provided, according to the present invention a process for the recovery of lactic acid from aqueous solutions containing at least one water-soluble lactate salt and having a pH of about between 4 and 14, comprising the steps of: a) contacting said aqueous solution with a cation exchanger which is at least partially in its acid form, said cation exchanger being water immiscible in both acid and salt form, whereby ion exchange is effected, protons are transferred from said cation exchanger to the aqueous solution to acidulate it and to form lactic acid therein and cations from said aqueous solution are bound by said cation exchanger; b) reacting said cations carrying cation exchanger to convert it into a cation exchanger which is at least partially in its acid form and to a second product, which second product is basic and comprises the cation of said salt; and c) recovering lactic acid from said lactic acid-containing acidulated aqueous solution by methods known per se.

As will be realized in accordance with the present invention, said cation exchanger can be a liquid or solid cation exchanger.

Thus, on contacting the lactate salt-containing solution with the cation exchanger in its acid form an ion exchange is effected. Protons from the

cation exchanger transfer into the aqueous solution where they bind with the lactate anions to form lactic acid. The cations of the lactate salt transfer at the same time to the cation exchanger and transform it into its salt form.

Solid cation exchangers carrying functional groups such as carboxyl or sulfone of the kind used, for example, for de-ionizing solutions, are suitable for the process. So are water-immiscible extractants such as fatty acids, alpha- or beta-halo carboxylic acids, sulfonic acids and mono- or di-esters of phosphoric acid. The cation exchanger salts formed are water immiscible as well, so that, unlike in the case of acidulating by a mineral acid, no salt is added to the broth. The cation exchanger in the acid form needs to be regenerated and is therefore preferably of a weak to medium acidity. It was found that in certain cases highly efficient acidulation is achievable by use of cation exchangers which are significantly weaker acids than lactic acid.

The acid/base properties of water soluble acids or bases are easily determined by their degree of dissociation in aqueous solution. The acid/base properties of water immiscible compounds are determined indirectly through their interaction with solutes in an aqueous solution. Thus the apparent acidity of various liquid or solid cation exchangers can be compared by contacting them with aqueous solutions of NaCl and determining the pH of the aqueous solution in equilibrium. The lower the pH, the stronger the apparent acidity of the cation exchanger. For comparing cation exchangers of relatively low acidity, equilibration with base solutions is preferred. Analogously, the basicity of water immiscible anion exchangers is determined by equilibration with aqueous solutions of salts or acids. Unlike in the case of water soluble acids and bases, the apparent acid/base properties found for water immiscible compounds are determined in addition to the intrinsic

properties of the anion/cation exchanger, by the method of measurement, by phenomena such as steric hindrance, and by the medium (in the case of liquid exchangers).

The salt form of the water immiscible cation exchanger can readily be treated to convert it back to its acid form. This can be achieved by contact with a solution of an acid or an acidic salt, preferably one that is stronger than the cation exchanger. Operating this way consumes a strong acid and could therefore be considered as an indirect acidulation of the lactate salt via a water immiscible cation exchanger. Unlike in the case of direct acidulation by adding a water soluble acid, no salt is formed in the aqueous solution in the case of indirect acidulation and one can use the preferred amine base extractants for the recovery of the liberated acid. Yet an acid is consumed and a by-product salt is formed. There are various ways to split this by-product salt. For example, an acidic ammonium salt of a di- or triprotic acid, e.g., NH_4HSO_4 , could be used as the regenerant of the cation exchanger in an ammonium form. The resulting ammonium sulfate decomposes thermally to ammonia to be reused, and to ammonium bisulfate, which is the acidulant. As long as the lactate is an ammonium lactate the regenerant could be NaHSO_4 or any other acidic sulfate salt, MHSO_4 , which is easy to work with. A metal M that forms MNH_4SO_4 of relatively low solubility is preferable, as it lowers the energy costs related to water evaporation during the thermal decomposition of the salt.

In a preferred embodiment the salt of the cation exchanger is decomposed to reform the acid form and a second product which is basic. An example is the case where the lactate salt is ammonium lactate and an ammonium salt of the water immiscible cation exchanger is formed. The latter

can be decomposed thermally to the cation exchanger in its acid form and to ammonia. Conducting the thermal decomposition at sub-atmospheric conditions or by transfer of a carrier gas helps in shifting the reaction in the desired direction. Steam and CO_2 are among the suitable carrier gases. Compared to the possibility of decomposition of a salt formed on regenerating of the acid form of the cation exchanger by an aqueous solution of an acid, direct decomposition saves on energy consumption for water evaporation. In addition, for a liquid cation exchanger, the decomposition can be assisted by changing the medium/solvent of the salt prior to its decomposition. An alternative to distillation of the second product is the precipitation thereof. Thus, thermal hydrolysis of calcium salts of the cation exchanger forms calcium hydroxide, or if conducted in the presence of CO_2 , CaCO_3 . The crystallization energy of these compounds assists the salt decomposition.

In a further preferred embodiment the second product is basic and can be reused as a neutralizing agent in fermentation. Thus, the lactate salt-containing aqueous solution could be a fermentation broth after removal of the biomass and possibly also after some additional pretreatments. Alternatively, it could be a stream obtained on recovery of lactic acid from broth treated by other methods. If ammonia is used for pH adjustment in the fermentation (i.e. used as the neutralizing agent there), the lactate salt in the broth will be primarily ammonium lactate. Acidulation by water immiscible cation exchanger would convert the latter from its acid form to its ammonium salt. Thermal decomposition of that ammonium salt reforms the cation exchanger in its acid form and forms a second product, ammonia which is basic. In fact the neutralizing agent is regenerated and can be reused in the fermentation. Thereby, the process avoids the consumption of stoichiometric amounts of a neutralizing base and of an acidulant and the formation of a

stoichiometric amount of a by-product salt. Examples for other basic, second decomposition products suitable for reuse in adjusting the pH in fermentation are calcium hydroxide or carbonate and sodium hydroxide, bicarbonate or carbonate resulting from applying the process to calcium lactate or sodium lactate-containing solutions respectively.

The lactic acid in the aqueous phase resulting from the acidulation by the water immiscible cation exchanger is mostly in its free, non-dissociated form. The aqueous solution still comprises most of the impurities it had prior to the acidulation and purification of the lactic acid may be required. That can be effected by one of the very well known methods for purifying lactic acid, including distilling the acid or an ester thereof, adsorption on a solid anion exchanger and solvent extraction. Suitable extractants are solvents such as alkanols, esters, ketones, etc., or extractants comprising water immiscible amines as the main active components. The latter are also considered liquid anion exchangers. Out of these two groups, the amine-based ones are more attractive for several reasons: (i) they are more selective and would therefore provide for higher product purity, (ii) their extraction capacity is higher and therefore the extractant flow will be lower, and (iii) the amine-based extractants show the temperature sensitivity of the extraction and therefore provide for the "uphill pumping" through back-extraction at a temperature which is higher than that of the extraction.

Suitable amines are primary, secondary or tertiary amines with a total carbon atom number of at least 18. Their concentration in the extractant is preferably above 0.5 mole/Kg and more preferably between 0.7 and 1.5 mole/Kg. The upper limit is determined by the viscosity and therefore dependent on the lactic acid concentration in the lactic acid-loaded extractant

(extract) and on the temperature. The diluent for the amine can comprise a variety of solvents such as kerosene, esters, ketones, aldehydes, ethers, alkanols, etc. Polar solvents enhance the extraction efficiency of the extractant due to their effect on the apparent basicity (and are therefore referred to as enhancers). The apparent basicity of the extractant can be increased by 1 to 2 pKa units by adding a suitable enhancer in an amount equivalent to more than 1 mole of enhancer to 1 mole of the amine in the extractant.

Unlike in the cases of salt splitting according to US 5,132,456, US 5,510,526 and others, where no acidulant is added, or where the acidulant is, in fact, a very weak acid, CO₂, the extractant or the anion exchanger in the present invention can be a relatively weak one. Weaker extractants or anion exchangers provide for easier recovery of the separated lactic acid. That is particularly important when the lactic acid is recovered from the extractant or from the water immiscible anion exchanger by back-extraction or by desorption with water. The weaker the extractant or the anion exchanger, the more concentrated will the aqueous product of the back-extraction (back-extract) or desorption (eluate) be. Thus, in the case of extraction by an amine-based extractant, tertiary amines are preferred over primary and secondary amines, and the enhancer content is preferably relatively low. The preferred apparent basicity of the extractant or the anion exchanger is less than 6 and more preferably less than 4.5. Alternatively, in an amine-based extractant the enhancer content in the extraction step is quite high so that the apparent basicity is higher and some of the enhancer is removed from the extract prior to the back-extraction.

Recovery of the lactic acid can be effected after the acidulation and possibly also after the separation of the water immiscible cation exchanger. Alternatively, the recovery of the lactic acid is conducted simultaneously with the acidulation so that both the water immiscible cation exchanger in its acid form and the water immiscible anion exchanger in its free base form are contacted with the lactic acid-containing solution. There are several known arrangements that allow such simultaneous contacting. In one of them the contact is effected in a unit which comprises at least two compartments. In one compartment a liquid cation exchanger is mixed with the lactate salt-containing aqueous solution, while the liquid anion exchanger is situated in or flowing through the other compartment. The two compartments are separated by a membrane that blocks transport of organic phase through it. There is no need to block water or cations. The membrane should let lactic acid through. Most anion exchange membranes and dense neutral hydrophilic membranes are suitable.

Alternatively, one compartment comprises a liquid cation exchanger and the other comprises a mixture of the lactate salt solution and a liquid anion exchanger. In that case the membrane between the compartments could be a cation exchange membrane or a dense neutral hydrophilic one. In a third option there are at least three compartments through which three streams are flowing: (I) the liquid cation exchanger, (ii) the lactate salt-containing aqueous solution, and (iii) the liquid anion exchanger. (I) and (ii) are separated by a cation exchange membrane or a dense neutral hydrophilic membrane, while (ii) and (iii) are separated by an anion exchange membrane (of the type that blocks cations, but allows protons through), or a dense neutral hydrophilic membrane. In some of these embodiments a solid cation

exchanger could replace the liquid cation exchanger and/or a solid anion exchanger can replace the liquid anion exchanger.

Alternatively to a simultaneous contact with both the cation exchanger and the anion exchanger, the lactate salt-containing solution could be recycled between the two. Thus, it can be contacted with the cation exchanger for partial acidulation, then contacted with the anion exchanger for recovery of some of the free acid, then recycled to the contact with the cation exchanger and so on.

Operating the acidulation by the cation exchanger separately from the recovery of the lactic acid results in a build-up of lactic acid in the aqueous solution. This build-up hinders further acidulation, and in order to reach a nearly complete acidulation, the acidity of the cation exchanger should be similar to or higher than that of lactic acid. Simultaneous contact with, or recycle between, a cation exchanger and an anion exchanger provides for removal of the lactic acid formed on the acidulation and thereby avoids the build-up of the acid in the aqueous solution. As a result, one can use a cation exchanger with a low apparent acidity, lower than that of lactic acid. In this case the decomposition of the salt form of the cation exchanger into the cation exchanger in the acid form and a second basic product is easier.

While the invention will now be described in connection with certain preferred embodiments in the following examples so that aspects thereof may be more fully understood and appreciated, it is not intended to limit the invention to these particular embodiments. On the contrary, it is intended to cover all alternatives, modifications and equivalents as may be included within the scope of the invention as defined by the appended claims. Thus,

the following examples which include preferred embodiments will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purposes of illustrative discussion of preferred embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of formulation procedures as well as of the principles and conceptual aspects of the invention.

Example 1

Aqueous solutions containing 30% ammonium lactate (initial pH=5.85) are equilibrated at ambient temperature with di-(2-ethyl hexyl) phosphoric acid (DEHPA) at various organic to aqueous ratios. The pH values of the resulting aqueous phase are determined: they are 4.9, 4.1 and 3.2 for organic to aqueous wt/wt ratios of 0.5:1, 1:1 and 3:1 respectively.

In a similar experiment 30% ammonium lactate solutions are contacted with dinonyl naphthalene sulfonic acid (obtained from King Industries as 50% solution in Norpar 12). The pH of the aqueous solutions in equilibrium are 5.1 and 4.5 for organic to aqueous wt/wt ratios of 0.5:1 and 1:1 respectively.

Lowering the pH in contact with the water immiscible cation exchangers is a result of removing ammonium cations from the solution through binding to the cation exchangers and thereby forming lactic acid in said aqueous solution.

Example 2

12.0g aqueous solution containing 0.49 mol/Kg sodium lactate (total of 5.9 mmol lactate) is contacted in a beaker with 1.09g dry cation exchanger Dowex 50x in its acid form (cation exchange capacity of 4.6 equivalent per gram dry). After shaking at ambient temperature for 2 hours, the solution was separated and analyzed for lactic acid by titration. 3.3 equivalents were found indicating conversion of 56% of the sodium lactate to lactic acid through cation exchange.

Example 3.

18.8 aqueous solution containing 2.4 mol/Kg ammonium lactate is equilibrated with 32.6g DEHPA at ambient temperature. An aqueous solution containing 0.97 mol/Kg lactic acid and ammonia containing organic phase are obtained. The organic phase is heated for 2 hours while nitrogen is bubbled through it. Most of its cation exchange capacity is thereby restored. Ammonia is condensed from the vapor phase. 12.3g of the lactic acid containing aqueous phase is equilibrated at ambient temperature with 47g extractant containing 48 wt% tricaprylyl amine (Henkel's Alamine 336), 30% octanol and 22% kerosene. 97% of the lactic acid values in the aqueous phase are extracted into the organic phase. Back-extraction with water at 140°C transfers more than 90% of the extracted acid into the obtained aqueous solution.

Example 4.

The following experiment tested simultaneous contacting of the lactic acid salt-containing aqueous solution with a liquid cation exchanger and a liquid anion exchanger. A three-compartment unit was used. Through one of the compartments a liquid cation exchanger was transferred. This compartment was separated by a membrane from the middle compartment, through which an aqueous solution of lactate salt was flowing. This compartment was separated by a second membrane from a third compartment through which a liquid anion exchanger was transferred. The volumes of the compartments were 10, 5 and 10 ml, respectively. The volumes of all three solutions flowing between their compartments and reservoirs were 100 ml. The flow rates for all three solutions were 50 ml/min. The membranes' working areas were 10^2 cm.

The cation exchanger used was 1.2 mol/kg solution of DEHPA in kerosene. The anion exchanger was a solution containing 1.2 mol/kg Alamine 336 + 20% octanol in kerosene. The aqueous solutions were of 1.0 mol/kg sodium or ammonium lactate. The membranes situated between the cation exchanger and the aqueous solution were Neosepta CM-1 or CM-2 cation exchange membranes obtained from Tokayama Soda Co. Those situated between the aqueous solution and the anion exchanger were Neosepta ACH-45 or Neosepta AFX, both are anion exchange membranes obtained from Tokayama Soda Co, or Celgard 3400, a dense hydrophilic membrane obtained from Celanese Co.

The rates of cations transport into the cation exchanger and of the simultaneous transport of lactic acid into the anion exchanger were followed. The flow rates in all the combinations tested were typically higher than $3 \cdot 10^{-5}$ mol/m² sec.

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative examples and that the present invention may be embodied in other specific forms without departing from the essential attributes thereof, and it is therefore desired that the present embodiments and examples be considered in all respects as illustrative and not restrictive, reference being made to the appended claims, rather than to the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

WHAT IS CLAIMED IS:

1. A process for the recovery of lactic acid from aqueous solutions containing at least one water-soluble lactate salt and having a pH of about between 4 and 14, comprising the steps of;

a) contacting said aqueous solution with a cation exchanger which is at least partially in its acid form, said cation exchanger being water immiscible in both acid and salt form, whereby ion exchange is effected, protons are transferred from said cation exchanger to the aqueous solution to acidulate it and to form lactic acid therein and cations from said aqueous solution are bound by said cation exchanger to form a cations carrying cation exchanger;

b) reacting said cations carrying cation exchanger to convert it into a cation exchanger which is at least partially in its acid form and to a second product, which second product is basic and comprises the cation of said salt; and

c) recovering lactic acid from said lactic acid-containing acidulated aqueous solution by methods known per se.

2. A process according to claim 1, wherein said cation exchanger is a liquid cation exchanger.

3. A process according to claim 1, wherein said cation exchanger is a solid cation exchanger.

4. A process according to claim 1, wherein said reaction in said step (b) is a decomposition reaction.

5. A process according to claim 1, wherein said lactic acid is recovered from said lactic acid-containing acidulated aqueous solution simultaneously with the acidulation thereof.

6. A process according to claim 1, wherein said lactic acid is recovered from said lactic acid-containing acidulated aqueous solution after the acidulation of said solution.

7. A process according to claim 1, wherein said second product is used as a neutralizing agent in fermentation.

8. A process according to claim 1, wherein said recovery of said lactic acid from the acidulated aqueous solution is effected by contacting said solution with a lactic acid extractant.

9. A process according to claim 1, wherein said recovery of said lactic acid from the acidulated aqueous solution is effected by contacting said solution with a lactic acid absorbent.

10. A process according to claim 1, wherein said recovery of said lactic acid from the acidulated aqueous solution is effected by contacting said solution with an anion exchanger which is at least partially in its free base form, which anion exchanger is water immiscible in both base and salt form.

11. A process according to claim 10 wherein said anion exchanger is a liquid anion exchanger.

AMENDED SHEET

12. A process according to claim 10, wherein said anion exchanger is a solid anion exchanger.

13. A process according to claim 10, wherein said anion exchanger, in its free base form has an apparent basicity corresponding to pKa of not higher than 6.

14. A process according to claim 10, wherein said anion exchanger, in its free base form has an apparent basicity corresponding to pKa of not higher than 4.5.

15. A process according to claim 10, wherein said cation exchanger in its at least partially acid form and said anion exchanger in its at least partially free base form are simultaneously contacted with said lactic acid salt-containing aqueous solution.

16. A process according to claim 10, wherein said cation exchanger in its at least partially acid form and said anion exchanger in its at least partially free base form are repeatedly alternately contacted with said lactic acid salt-containing aqueous solution.

17. A process according to claim 10, wherein said anion exchanger is separated from said aqueous solution by an anion exchange membrane.

18. A process according to claim 10, wherein said anion exchanger is separated from said aqueous solution by a dense neutral hydrophilic membrane.

AMENDED SHEET

26. A process according to claim 24, wherein hydrolysis is conducted at a temperature higher than 80°C.
27. A process according to claim 4, wherein said second decomposition product is transferred into a vapor phase.
28. A process according to claim 4, wherein said lactic acid salt is ammonium lactate and said second decomposition product is ammonia.
29. A process according to claim 1, wherein said lactate salt is a product of fermentation.
30. A process according to claim 1, wherein the reaction of step (b) is conducted in a CO₂ containing atmosphere.
31. A process according to claim 1, wherein recovery of lactic acid from said acidulated aqueous solution is effected by distillation.
32. A process according to claim 10, wherein said lactic acid is recovered from said anion exchanger.
33. A process according to claim 1, wherein recovery of lactic acid from said acidulated aqueous solution is effected by distillation of its ester.
34. A process for the recovery of lactic acid from aqueous solutions containing at least one water-soluble lactate salt and having a pH of about between 4 and 14, comprising the steps of;
- a) contacting said aqueous solution with a cation exchanger which is at least partially in its acid form, said cation exchanger being water immiscible in both acid and salt form, whereby ion exchange is effected, protons are transferred from said cation exchanger to the aqueous solution to acidulate it and to form lactic acid therein and cations from said aqueous solution are bound by said cation exchanger to form a cations-carrying cation exchanger;
 - b) simultaneously recovering lactic acid from said lactic acid-containing acidulated aqueous solution by methods known per se; and
 - c) reacting said cations-carrying cation exchanger to convert it into a cation exchanger which is at least partially in its acid form and to a second product, which second product is basic and comprises the cations of said salt.

AMENDED SHEET

A PROCESS FOR THE RECOVERY OF LACTIC ACID

ABSTRACT OF THE DISCLOSURE

The invention provides a process for the recovery of lactic acid from aqueous solutions containing at least one water-soluble lactate salt and having a pH of about between 4 and 14, comprising the steps of: contacting said aqueous solution with a cation exchanger which is at least partially in its acid form, said cation exchanger being water immiscible in both acid and salt form, whereby ion exchange is effected, protons are transferred from the cation exchanger to the aqueous solution to acidulate it and to form lactic acid therein and cations from the aqueous solution are bound by the cation exchanger; reacting the cations carrying cation exchanger to convert it into a cation exchanger which is at least partially in its acid form and to a second product, which second product is basic and comprises the cation of the salt; and recovering lactic acid from the lactic acid-containing acidulated aqueous solution by methods known per se.

COMBINED DECLARATION AND POWER OF ATTORNEY

(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL, DIVISIONAL,
CONTINUATION, OR C-I-P)

As a below named inventor, I hereby declare that:

TYPE OF DECLARATION

This declaration is of the following type:

(check one applicable item below)

- ☐ original.
☐ design.
☐ supplemental.

NOTE: *If the declaration is for an International Application being filed as a divisional, continuation or continuation-in-part application, do not check next item; check appropriate one of last three items.*

- ☒ national stage of PCT.

NOTE: *If one of the following 3 items apply, then complete and also attach ADDED PAGES FOR DIVISIONAL, CONTINUATION OR C-I-P.*

NOTE: *See 37 CFR 1.63(d) (continued prosecution application) for use of a prior nonprovisional application declaration in the continuation or divisional application being filed on behalf of the same or fewer of the inventors named in the prior application.*

- ☐ divisional.
☐ continuation.

NOTE: *Where an application discloses and claims subject matter not disclosed in the prior application, or a continuation or divisional application names an inventor not named in the prior application, a continuation-in-part application must be filed under 37 CFR 1.53(b) (application filing requirements-nonprovisional application).*

- ☐ continuation-in-part (C-I-P).

INVENTORSHIP IDENTIFICATION

WARNING: *If the inventors are each not the inventors of all the claims, an explanation of the facts, including the ownership of all the claims at the time the last claimed invention was made, should be submitted.*

My residence, post office address and citizenship are as stated below, next to my name. I believe that I am the original, first and sole inventor (*if only one name is listed below*) or an original, first and joint inventor (*if plural names are listed below*) of the subject matter that is claimed, and for which a patent is sought on the invention entitled:

TITLE OF INVENTION

A Process for the Recovery of Lactic Acid

SPECIFICATION IDENTIFICATION

The specification of which:

(complete (a), (b), or (c))

(a) ☒ is attached hereto.

NOTE: "The following combinations of information supplied in an oath or declaration filed on the application filing date with a specification are acceptable as minimums for identifying a specification and compliance with any one of the items below will be accepted as complying with the identification requirements of 37 CFR 1.63:

"(1) name of inventor(s), and reference to an attached specification which is both attached to the oath or declaration at the time of execution and submitted with the oath or declaration on filing;

"(2) name of inventor(s), and attorney docket number which was on the specification as filed; or

"(3) name of inventor(s), and title which was on the specification as filed."

Notice of July 13, 1995 (1177 O.G. 60).

(b) ☐ was filed on _____ as ☐ Serial No. 0 / _____ or
☐ _____ and was amended on _____ (if applicable).

NOTE: Amendments filed after the original papers are deposited with the PTO that contain new matter are not accorded a filing date by being referred to in the declaration. Accordingly, the amendments involved are those filed with the application papers or, in the case of a supplemental declaration, are those amendments claiming matter not encompassed in the original statement of invention or claims. See 37 CFR 1.67.

NOTE: "The following combinations of information supplied in an oath or declaration filed after the filing date are acceptable as minimums for identifying a specification and compliance with any one of the items below will be accepted as complying with the identification requirement of 37 CFR 1.63:

"(1) name of inventor(s), and application number (consisting of the series code and the serial number; e.g., 08/123,456);

"(2) name of inventor(s), serial number and filing date;

"(3) name of inventor(s) and attorney docket number which was on the specification as filed;

"(4) name of inventor(s), title which was on the specification as filed and filing date;

"(5) name of inventor(s), title which was on the specification as filed and reference to an attached specification which is both attached to the oath or declaration at the time of execution and submitted with the oath or declaration; or

"(6) name of inventor(s), title which was on the specification as filed and accompanied by a cover letter accurately identifying the application for which it was intended by either the application number (consisting of the series code and the serial number; e.g., 08/123,456), or serial number and filing date. Absent any statement(s) to the contrary, it will be presumed that the application filed in the PTO is the application which the inventor(s) executed by signing the oath or declaration."

Notice of July 13, 1995 (1177 O.G. 60).

- (c) ☒ was described and claimed in PCT International Application No. US97/17774
filed on October 2, 1997 and as amended under PCT Article 19 on _____
(if any).

SUPPLEMENTAL DECLARATION (37 CFR 1.67(b))

(complete the following where a supplemental declaration is being submitted)

☐ I hereby declare that the subject matter of the

- ☐ attached amendment
☐ amendment filed on _____

was part of my/our invention and was invented before the filing date of the original application,
above identified, for such invention.

ACKNOWLEDGMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified
specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in
37, Code of Federal Regulations, § 1.56,

(also check the following items, if desired)

- ☐ and which is material to the examination of this application, namely, information where
there is a substantial likelihood that a reasonable Examiner would consider it important
in deciding whether to allow the application to issue as a patent, and
- ☐ in compliance with this duty, there is attached an information disclosure
statement, in accordance with 37 CFR 1.98.

PRIORITY CLAIM (35 U.S.C. § 119(a)-(d))

NOTE *"The claim to priority need be in no special form and may be made by the attorney or agent if the foreign application is referred to in the oath or declaration as required by § 1.63. The claim for priority and the certified copy of the foreign application specified in 35 U.S.C. § 119(b) must be filed in the case of an interference (§ 1.630), when necessary to overcome the date of a reference relied upon by the examiner, when specifically required by the examiner, and in all other situations, before the patent is granted. If the claim for priority or the certified copy of the foreign application is filed after the date the issue fee is paid, it must be accompanied by a petition requesting entry and by the fee set forth in § 1.17(i). If the certified copy is not in the English language, a translation need not be filed except in the case of interference; or when necessary to overcome the date of a reference relied upon by the examiner; or when specifically required by the examiner, in which event an English language translation must be filed together with a statement that the translation of the certified copy is accurate." 37 CFR 1.55(a).*

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

(complete (d) or (e))

- (d) ☐ no such applications have been filed.
(e) ☒ such applications have been filed as follows.

NOTE *Where item (c) is entered above and the International Application which designated the U.S. itself claimed priority check item (e), enter the details below and make the priority claim.*

**PRIOR FOREIGN/PCT APPLICATION(S) FILED WITHIN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS APPLICATION
AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. § 119(a)-(d)**

| COUNTRY (OR INDICATE IF PCT) | APPLICATION NUMBER | DATE OF FILING DAY, MONTH, YEAR | PRIORITY CLAIMED UNDER 35 USC 119 |
|---------------------------------|--------------------|------------------------------------|---|
| ISRAEL | 119389 | 9 OCTOBER 1996 | <input checked="" type="checkbox"/> YES <input type="checkbox"/> NO |
| | | | <input type="checkbox"/> YES <input type="checkbox"/> NO |
| | | | <input type="checkbox"/> YES <input type="checkbox"/> NO |
| | | | <input type="checkbox"/> YES <input type="checkbox"/> NO |
| | | | <input type="checkbox"/> YES <input type="checkbox"/> NO |

**CLAIM FOR BENEFIT OF PRIOR U.S. PROVISIONAL APPLICATION(S)
(35 U.S.C. § 119(e))**

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

PROVISIONAL APPLICATION NUMBER

FILING DATE

**CLAIM FOR BENEFIT OF EARLIER U.S./PCT APPLICATION(S)
UNDER 35 U.S.C. § 120**

☐ The claim for the benefit of any such applications are set forth in the attached ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR CONTINUATION-IN-PART (C-I-P) APPLICATION.

**ALL FOREIGN APPLICATION(S), IF ANY, FILED MORE THAN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION**

NOTE: If the application filed more than 12 months from the filing date of this application is a PCT filing forming the basis for this application entering the United States as (1) the national stage, or (2) a continuation, divisional, or continuation-in-part, then also complete ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR C-I-P APPLICATION for benefit of the prior U.S. or PCT application(s) under 35 U.S.C. § 120.

POWER OF ATTORNEY

I hereby appoint the following practitioner(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

(list name and registration number)

JOSEPH H. HANDELMAN, 26179

RICHARD P. BERG, 28145

JOHN RICHARDS, 31053

JULIAN H. COHEN, 20302

RICHARD J. STREIT, 25765

WILLIAM R. EVANS, 25858

PETER D. GALLOWAY, 27885

JANET I. CORD, 33778

IAN C. BAILLIE, 24090

CLIFFORD J. MASS, 30086

THOMAS F. PETERSON, 24790

(Check the following item, if applicable)

☐ Attached, as part of this declaration and power of attorney, is the authorization of the above-named practitioner(s) to accept and follow instructions from my representative(s).

SEND CORRESPONDENCE TO

DIRECT TELEPHONE CALLS TO:

(Name and telephone number)

Ladas & Parry
26 West 61st Street
New York, N.Y. 10023

DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon

SIGNATURE(S)

NOTE: Carefully indicate the family (or last) name, as it should appear on the filing receipt and all other document.

Full name of sole or first inventor

1-00 AHARON MEIR EYAL
(Given Name) (Middle Initial or Name) Family (Or Last Name)

Inventor's signature X A.H. Gof

Date March 23 1999 Country of Citizenship ISRAEL

Residence 32 Baitar Street, Jerusalem 93380 ISRAEL ILX

Post Office Address Same as above

Full name of second joint inventor, if any

PONNAMPALAM BLANKOVAN
(Given Name) (Middle Initial or Name) Family (Or Last Name)

Inventor's signature _____

Date _____ Country of Citizenship UNITED STATES

Residence 2365 Club Meridian Drive, Okemos, MI 48864 United States of America

Post Office Address Same as above

Full name of third joint inventor, if any

(Given Name) (Middle Initial or Name) Family (Or Last Name)

Inventor's signature _____

Date _____ Country of Citizenship _____

Residence _____

Post Office Address _____

*(check proper box(es) for any of the following added page(s)
that form a part of this declaration)*

☐ Signature for fourth and subsequent joint inventors. *Number of pages added* _____

* * *

☐ Signature by administrator(trix), executor(trix) or legal representative for deceased or incapacitated inventor. *Number of pages added* _____

* * *

☐ Signature for inventor who refuses to sign or cannot be reached by person authorized under 37 CFR 1.47. *Number of pages added* _____

* * *

☐ Added page for signature by one joint inventor on behalf of deceased inventor(s) where legal representative cannot be appointed in time. (37 CFR 1.47)

* * *

☐ Added pages to combined declaration and power of attorney for divisional, continuation, or continuation-in-part (C-I-P) application.

☐ Number of pages added _____

* * *

☐ Authorization of practitioner(s) to accept and follow instructions from representative.

*(If no further pages form a part of this Declaration,
then end this Declaration with this page and check the following item)*

☒ This declaration ends with this page.

COMBINED DECLARATION AND POWER OF ATTORNEY

(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL, DIVISIONAL,
CONTINUATION, OR C-I-P)

As a below named inventor, I hereby declare that:

TYPE OF DECLARATION

This declaration is of the following type:

(check one applicable item below)

- ☐ original.
☐ design.
☐ supplemental.

NOTE: *If the declaration is for an International Application being filed as a divisional, continuation or continuation-in-part application, do not check next item; check appropriate one of last three items.*

- ☒ national stage of PCT.

NOTE: *If one of the following 3 items apply, then complete and also attach ADDED PAGES FOR DIVISIONAL, CONTINUATION OR C-I-P.*

NOTE: *See 37 CFR 1.63(d) (continued prosecution application) for use of a prior nonprovisional application declaration in the continuation or divisional application being filed on behalf of the same or fewer of the inventors named in the prior application.*

- ☐ divisional.
☐ continuation.

NOTE: *Where an application discloses and claims subject matter not disclosed in the prior application, or a continuation or divisional application names an inventor not named in the prior application, a continuation-in-part application must be filed under 37 CFR 1.53(b) (application filing requirements-nonprovisional application).*

- ☐ continuation-in-part (C-I-P).

INVENTORSHIP IDENTIFICATION

WARNING: *If the inventors are each not the inventors of all the claims, an explanation of the facts, including the ownership of all the claims at the time the last claimed invention was made, should be submitted.*

My residence, post office address and citizenship are as stated below, next to my name. I believe that I am the original, first and sole inventor (*if only one name is listed below*) or an original, first and joint inventor (*if plural names are listed below*) of the subject matter that is claimed, and for which a patent is sought on the invention entitled:

TITLE OF INVENTION

A Process for the Recovery of Lactic Acid

SPECIFICATION IDENTIFICATION

The specification of which:

(complete (a), (b), or (c))

(a) ☒ is attached hereto.

NOTE: "The following combinations of information supplied in an oath or declaration filed on the application filing date with a specification are acceptable as minimums for identifying a specification and compliance with any one of the items below will be accepted as complying with the identification requirement of 37 CFR 1.63:

"(1) name of inventor(s), and reference to an attached specification which is both attached to the oath or declaration at the time of execution and submitted with the oath or declaration on filing;

"(2) name of inventor(s), and attorney docket number which was on the specification as filed; or

"(3) name of inventor(s), and title which was on the specification as filed."

Notice of July 13, 1995 (1177 O.G. 60).

(b) ☐ was filed on _____, as ☐ Serial No. 0 / _____ or
☐ _____ and was amended on _____ (if applicable).

NOTE: Amendments filed after the original papers are deposited with the PTO that contain new matter are not accorded a filing date by being referred to in the declaration. Accordingly, the amendments involved are those filed with the application papers or, in the case of a supplemental declaration, are those amendments claiming matter not encompassed in the original statement of invention or claims. See 37 CFR 1.67.

NOTE: "The following combinations of information supplied in an oath or declaration filed after the filing date are acceptable as minimums for identifying a specification and compliance with any one of the items below will be accepted as complying with the identification requirement of 37 CFR 1.63:

"(1) name of inventor(s), and application number (consisting of the series code and the serial number; e.g., 08/123,456);

"(2) name of inventor(s), serial number and filing date;

"(3) name of inventor(s) and attorney docket number which was on the specification as filed;

"(4) name of inventor(s), title which was on the specification as filed and filing date;

"(5) name of inventor(s), title which was on the specification as filed and reference to an attached specification which is both attached to the oath or declaration at the time of execution and submitted with the oath or declaration; or

"(6) name of inventor(s), title which was on the specification as filed and accompanied by a cover letter accurately identifying the application for which it was intended by either the application number (consisting of the series code and the serial number; e.g., 08/123,456), or serial number and filing date. Absent any statement(s) to the contrary, it will be presumed that the application filed in the PTO is the application which the inventor(s) executed by signing the oath or declaration."

Notice of July 13, 1995 (1177 O.G. 60).

- (c) ☒ [X] was described and claimed in PCT International Application No. US97/17774
filed on October 2, 1997 and as amended under PCT Article 19 on _____
(if any).

SUPPLEMENTAL DECLARATION (37 CFR 1.67(b))

(complete the following where a supplemental declaration is being submitted)

☐ [] I hereby declare that the subject matter of the

☐ [] attached amendment

☐ [] amendment filed on _____.

was part of my/our invention and was invented before the filing date of the original application,
above identified, for such invention.

ACKNOWLEDGMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified
specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in
37, Code of Federal Regulations, § 1.56,

(also check the following items, if desired)

- ☐ [] and which is material to the examination of this application, namely, information where
there is a substantial likelihood that a reasonable Examiner would consider it important
in deciding whether to allow the application to issue as a patent, and
- ☐ [] in compliance with this duty, there is attached an information disclosure
statement, in accordance with 37 CFR 1.98.

PRIORITY CLAIM (35 U.S.C. § 119(a)-(d))

NOTE *"The claim to priority need be in no special form and may be made by the attorney or agent if the foreign application is referred to in the oath or declaration as required by § 1.63. The claim for priority and the certified copy of the foreign application specified in 35 U.S.C. § 119(b) must be filed in the case of an interference (§ 1.630), when necessary to overcome the date of a reference relied upon by the examiner, when specifically required by the examiner, and in all other situations, before the patent is granted. If the claim for priority or the certified copy of the foreign application is filed after the date the issue fee is paid, it must be accompanied by a petition requesting entry and by the fee set forth in § 1.17(i). If the certified copy is not in the English language, a translation need not be filed except in the case of interference; or when necessary to overcome the date of a reference relied upon by the examiner; or when specifically required by the examiner, in which event an English language translation must be filed together with a statement that the translation of the certified copy is accurate." 37 CFR 1.55(a).*

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

(complete (d) or (e))

- (d) ☐ no such applications have been filed.
- (e) ☒ such applications have been filed as follows.

NOTE *Where item (c) is entered above and the International Application which designated the U.S. itself claimed priority check item (e), enter the details below and make the priority claim.*

**PRIOR FOREIGN/PCT APPLICATION(S) FILED WITHIN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS APPLICATION
AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. § 119(a)-(d)**

| COUNTRY (OR INDICATE IF PCT) | APPLICATION NUMBER | DATE OF FILING DAY, MONTH, YEAR | PRIORITY CLAIMED UNDER 35 USC 119 |
|---------------------------------|--------------------|------------------------------------|---|
| ISRAEL | 119389 | 9 OCTOBER 1996 | <input checked="" type="checkbox"/> YES <input type="checkbox"/> NO |
| | | | <input type="checkbox"/> YES <input type="checkbox"/> NO |
| | | | <input type="checkbox"/> YES <input type="checkbox"/> NO |
| | | | <input type="checkbox"/> YES <input type="checkbox"/> NO |
| | | | <input type="checkbox"/> YES <input type="checkbox"/> NO |

**CLAIM FOR BENEFIT OF PRIOR U.S. PROVISIONAL APPLICATION(S)
(35 U.S.C. § 119(e))**

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

PROVISIONAL APPLICATION NUMBER

FILING DATE

**CLAIM FOR BENEFIT OF EARLIER U.S./PCT APPLICATION(S)
UNDER 35 U.S.C. § 120**

- ☐ The claim for the benefit of any such applications are set forth in the attached ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR CONTINUATION-IN-PART (C-I-P) APPLICATION.

**ALL FOREIGN APPLICATION(S), IF ANY, FILED MORE THAN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION**

NOTE: If the application filed more than 12 months from the filing date of this application is a PCT filing forming the basis for this application entering the United States as (1) the national stage, or (2) a continuation, divisional, or continuation-in-part, then also complete ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR C-I-P APPLICATION for benefit of the prior U.S. or PCT application(s) under 35 U.S.C. § 120.

POWER OF ATTORNEY

I hereby appoint the following practitioner(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

(list name and registration number)

JOSEPH H. HANDELMAN, 26179

RICHARD P. BERG, 28145

JOHN RICHARDS, 31053

JULIAN H. COHEN, 20302

RICHARD J. STREIT, 25765

WILLIAM R. EVANS, 25858

PETER D. GALLOWAY, 27885

JANET I. CORD, 33778

IAN C. BAILLIE, 24090

CLIFFORD J. MASS, 30086

THOMAS F. PETERSON, 24790

(Check the following item, if applicable)

- ☐ Attached, as part of this declaration and power of attorney, is the authorization of the above-named practitioner(s) to accept and follow instructions from my representative(s).

SEND CORRESPONDENCE TO

DIRECT TELEPHONE CALLS TO:

(Name and telephone number)

Ladas & Parry
26 West 61st Street
New York, N.Y. 10023

DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon

*(check proper box(es) for any of the following added page(s)
that form a part of this declaration)*

☐ **Signature** for fourth and subsequent joint inventors. *Number of pages added* _____

* * *

☐ **Signature** by administrator(trix), executor(trix) or legal representative for deceased or incapacitated inventor. *Number of pages added* _____

* * *

☐ **Signature** for inventor who refuses to sign or cannot be reached by person authorized under 37 CFR 1.47. *Number of pages added* _____

* * *

☐ **Added page for signature** by one joint inventor on behalf of deceased inventor(s) where legal representative cannot be appointed in time. (37 CFR 1.47)

* * *

☐ **Added pages to combined declaration and power of attorney for divisional, continuation, or continuation-in-part (C-I-P) application.**

☐ **Number of pages added** _____

* * *

☐ **Authorization of practitioner(s) to accept and follow instructions from representative.**

*(If no further pages form a part of this Declaration,
then end this Declaration with this page and check the following item)*

☒ This declaration ends with this page.

SIGNATURE(S)

NOTE: Carefully indicate the family (or last) name, as it should appear on the filing receipt and all other document.

Full name of sole or first inventor

AHARON
(Given Name)MEIR
(Middle Initial or Name)EYAL
Family (Or Last Name)

Inventor's signature _____

Date _____ Country of Citizenship ISRAELResidence 32 Baitar Street. Jerusalem 93380 ISRAELPost Office Address Same as above

Full name of second joint inventor, if any

PONNAMPALAM
(Given Name)

(Middle Initial or Name)

ELANKOVAN
Family (Or Last Name)Inventor's signature X Ponnampalam ElankovanDate X 4-19-99 Country of Citizenship UNITED STATESResidence 2365 Club Meridian Drive. Okemos, MI 48864 United States of AmericaPost Office Address Same as above

Full name of third joint inventor, if any

(Given Name)

(Middle Initial or Name)

Family (Or Last Name)

Inventor's signature _____

Date _____ Country of Citizenship _____

Residence _____

Post Office Address _____